

Supporting Information

Efficient Synthesis of Narrowly Dispersed Brush Copolymers and Study of Their Assemblies: the Importance of Side Chain Arrangement

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Experimental Section

Materials. $(\text{H}_2\text{IMes})(\text{pyr})_2(\text{Cl})_2\text{RuCHPh}^1$, N-(hydroxyethyl)-*cis*-5-norbornene-exo-2,3-dicarboximide², and N-(pentynoyl decanyl)-*cis*-5-norbornene-exo-2,3-dicarboximide³ were prepared as described previously. The synthesis and characterization of PMA, PtBA, and PS MMs have been reported previously³ and the PnBA MM was synthesized in a similar manner. *n*-BA was passed through a column of basic alumina immediately before use. D, L-lactide was recrystallized from ethyl acetate three times. All other materials were obtained from commercial sources and used as received.

Synthesis of PLA macromonomers. A flame-dried Schlenk tube was charged with N-(hydroxyethyl)-*cis*-5-norbornene-exo-2,3-dicarboximide (54 mg, 0.26 mmol), D, L-lactide (1.5 g, 10.4 mmol), tin (II) 2-ethylhexanoate (2.1 mg, 5.2 μmol), and a stir bar. The tube was evacuated and backfilled with argon four times, and was then immersed in an oil bath at 120 °C. After 4h, the contents were cooled to room temperature, diluted with dichloromethane, and precipitated into acidic methanol. The MM was isolated by decanting the supernatant and drying *in vacuo*. ¹H NMR (500 MHz, CDCl_3): δ 1.24 (br d, 1H), 1.40-1.70 (br, 253H), 2.72 (br, 2H), 3.28 (br, 2H), 3.70-3.85 (m, 2H), 4.22-4.40 (m, 3H), 5.00-5.30 (m, 84H), 6.30 (br t, 2H). GPC-MALLS: $M_n = 7.0 \text{ kg/mol}$, $M_w/M_n = 1.12$.

General procedure for synthesis of brush block and random copolymers via ROMP of macromonomers. An oven-dried vial was charged with 100 mg MM for the first block and a stir bar. The vial was then degassed, and the desired amount of degassed anhydrous THF ($[\text{M}]_0 = 0.05\text{-}0.10 \text{ M}$) was added via syringe under an argon atmosphere to dissolve the MM. A stock solution of Ru catalyst in degassed anhydrous THF was prepared in a separate vial. The desired amount of catalyst was injected into the MM solution to initiate the polymerization. The reaction was allowed to proceed at room temperature for 20-30 min. After the first polymerization was complete, the desired amount of second MM was added as a solution in THF ($[\text{M}]_0 = 0.05\text{-}0.10 \text{ M}$). After 1h, the reaction mixture was quenched with one drop of ethyl vinyl ether. A sample was then withdrawn for GPC analysis without any purification. The block copolymer was isolated either by precipitating into cold methanol, or by simply drying *in vacuo*.

The random copolymers were synthesized using a similar procedure as the block copolymers, except that two types of MMs were added together in the reaction vial before catalyst injection.

Characterization. ^1H and ^{13}C NMR spectroscopy was recorded in CDCl_3 or $\text{DMF-}d_7$ using a Varian Mercury 300 or Varian Inova 500 spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protiated solvent signal as an internal standard.

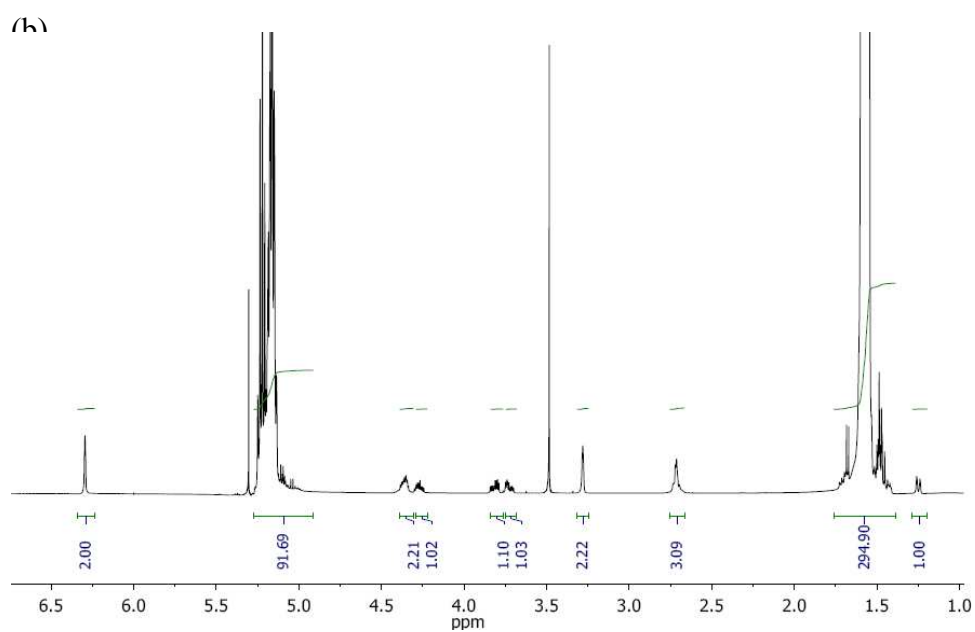
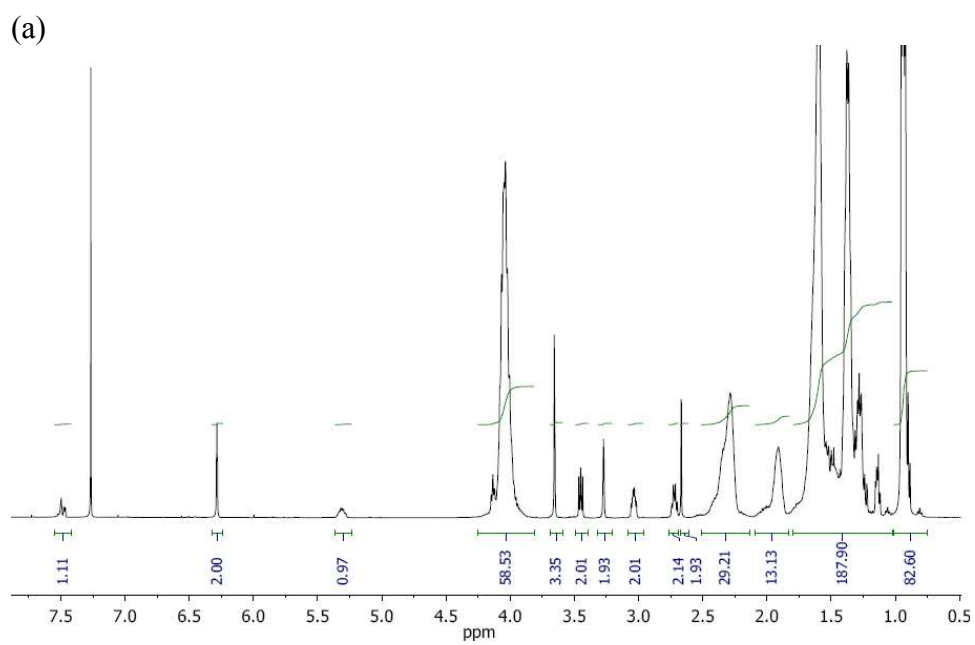
Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained for each injection by assuming 100% mass elution from the columns.

Atomic Force Microscopy (AFM) images were taken using a Nanoscope IV Scanning Probe Microscope Controller (Digital Instruments, Veeco Metrology Group) in tapping mode in air at room temperature using silicon tips (spring constant = 40-50 N/m, resonance frequency = 170-190 kHz, and tip radius of curvature <10 nm). The samples for imaging individual polymers were prepared by spin casting very dilute solutions (<0.01 wt%) in chloroform onto freshly cleaved mica at 1500 rpm. Thin film samples were prepared by spin casting solutions (2.5 wt%) in toluene onto Si(100) with a native oxide layer at 1500 rpm. A Gartner L116-C ellipsometer was used to measure the film thickness.

Differential Scanning Calorimetry (DSC) was performed on a Perkin-Elmer DSC 7. Samples were heated to 180 °C at 20 °C/min to erase any thermal history, then cooled to 0 °C at 20 °C/min, and reheated to 150 °C at 15 °C/min. The second heating scan was used to determine the T_g of PLA.

Small Angle X-ray Scattering (SAXS). Samples for SAXS were prepared by annealing polymers in vacuum (10 mTorr) at 110 °C for 12 h to form 1 mm thick disks and then sealing the samples between Kapton windows. Experiments were performed on beamline 27X-C at Brookhaven National Lab. The beamline was configured with an X-ray wavelength of 1.371 Å. Samples were corrected for transmission, thickness, empty cell,

and dark field scattering and radially averaged to produce 1D I vs. q plots. Temperature-dependent experiments were conducted by increasing temperature in 5 °C steps with 5 minutes of thermal equilibration after reaching each temperature before starting data acquisition.



(c)

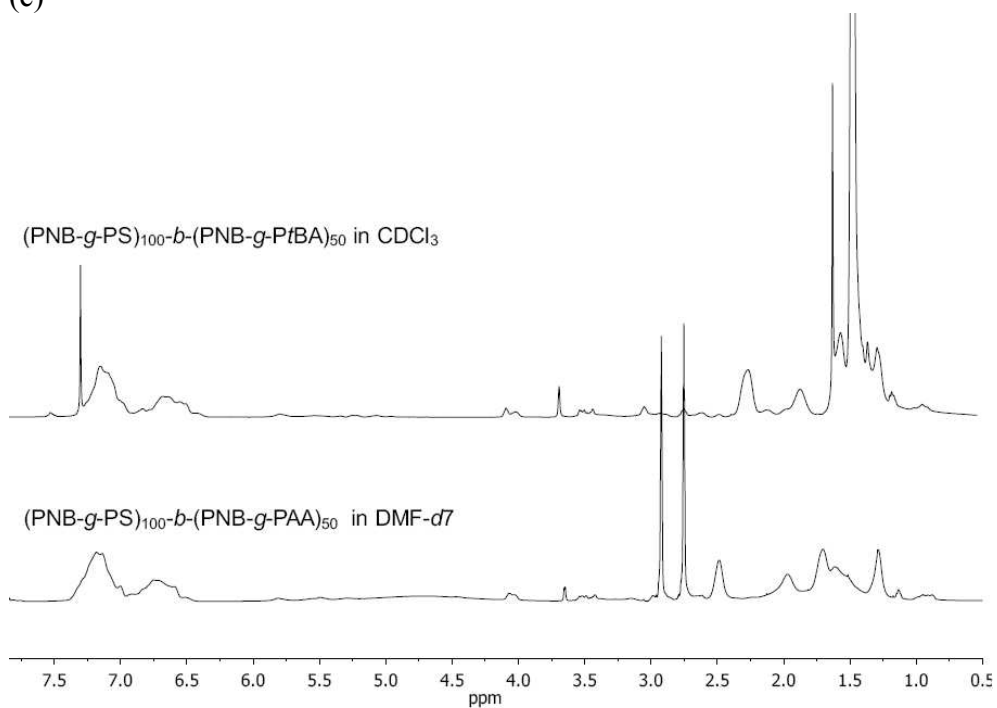
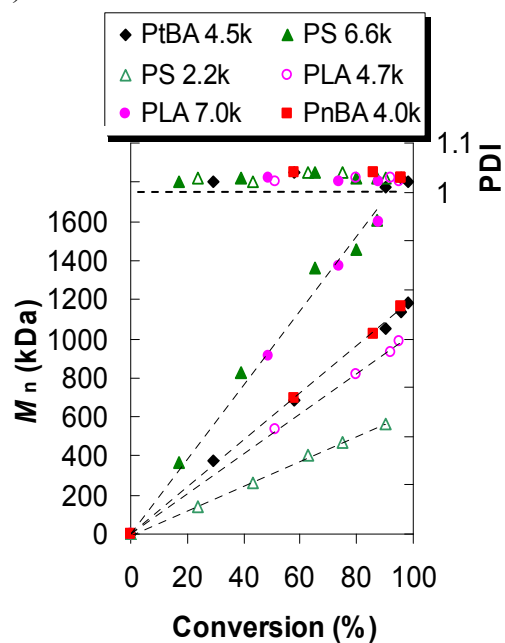


Figure S1. ¹H NMR spectra of (a) macromonomer NB(*Pn*BA)4.0k; (b) macromonomer NB(PLA)7.0k; (c) (PNB-*g*-PS)₁₀₀-b-(PNB-*g*-PtBA)₅₀ and hydrolyzed (PNB-*g*-PS)₁₀₀-b-(PNB-*g*-PAA)₅₀.

(a)



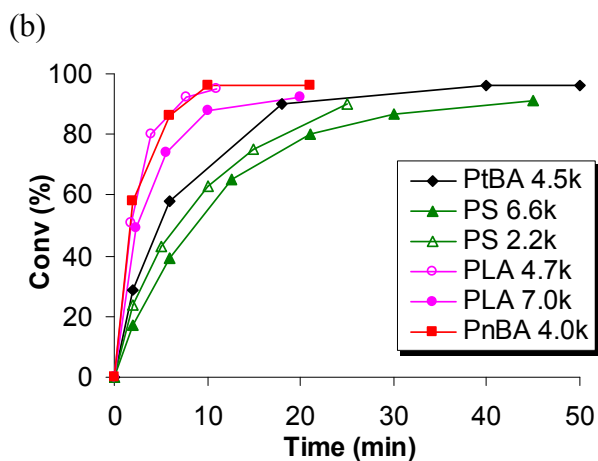
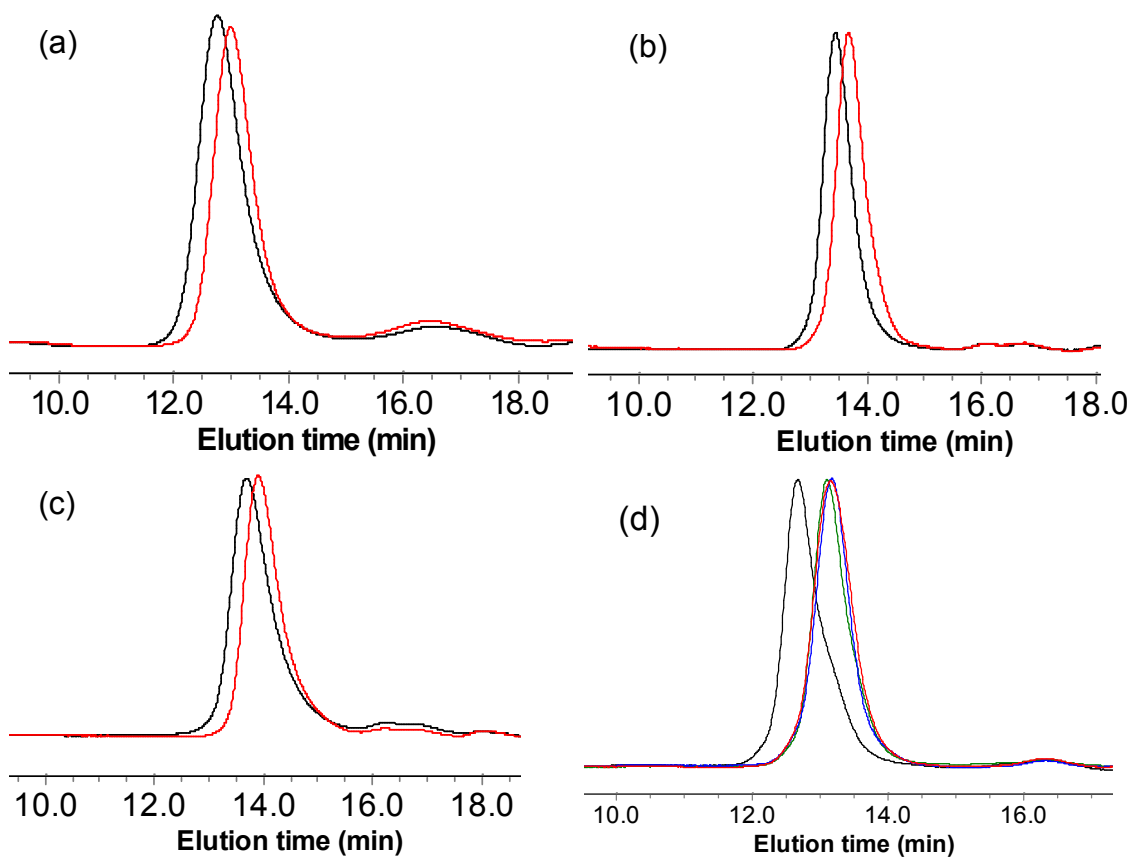


Figure S2. ROMP of MMs: (a) Dependence of M_n , GPC and PDI on conversion; (b) MM conversion vs time. Conditions: $[MM]_0 = 0.05M$ in THF at room temperature, $[MM/C]_0 = 200$.



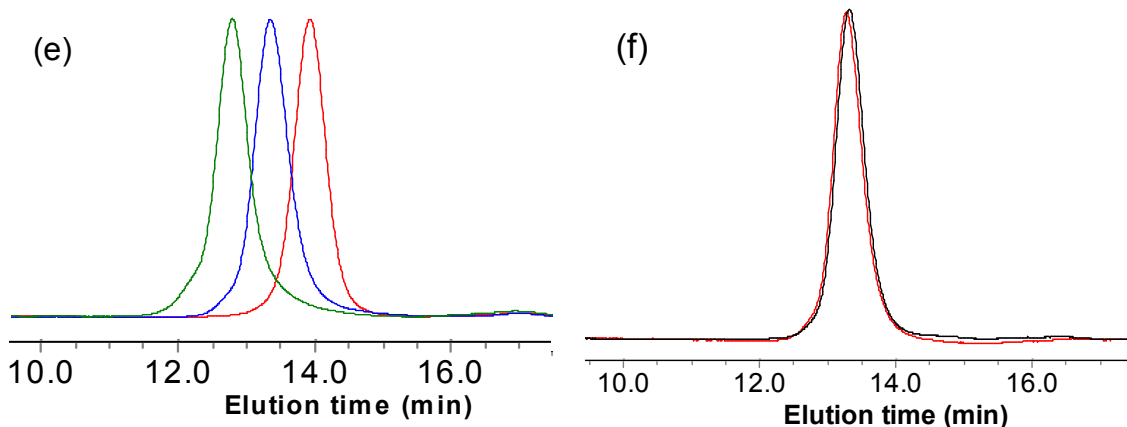
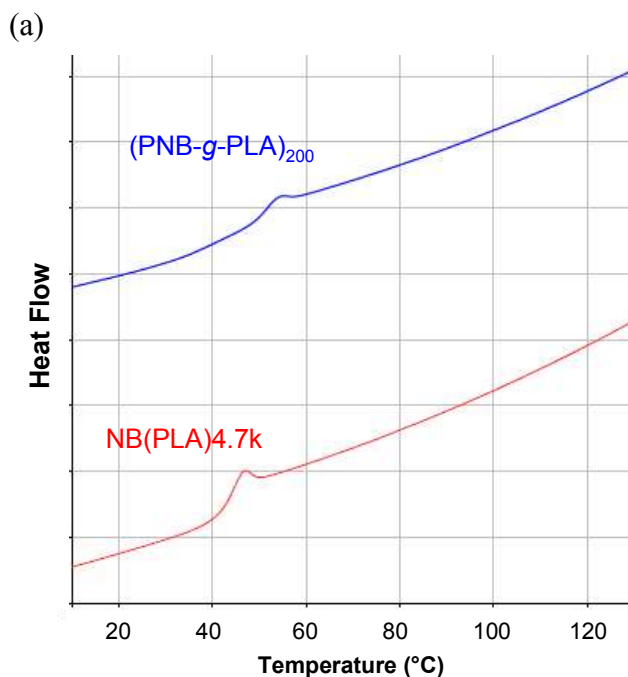


Figure S3. GPC RI traces of brush copolymers in Table 2. All the traces were obtained from crude polymers after ROMP without any purification. (a) red: entry 1 in table 1 (PNB-*g*-PS)₄₀-*b*-(PNB-*g*-PnBA)₇₀; black: entry 2 in table 1 (PNB-*g*-PS)₄₀-*b*-(PNB-*g*-PnBA)₂₀₀; (b) red: entry 3 in table 1 (PNB-*g*-PtBA)₁₀₀-*b*-(PNB-*g*-PnBA)₁₀₀; black: entry 4 in table 1 (PNB-*g*-PtBA)₁₀₀-*b*-(PNB-*g*-PnBA)₂₀₀; (c) red: entry 5 in table 1 (PNB-*g*-PS)₅₀-*b*-(PNB-*g*-PtBA)₅₀; black: entry 6 in table 1 (PNB-*g*-PS)₁₀₀-*b*-(PNB-*g*-PtBA)₅₀; (d) blue: entry 7 in table 1 (PNB-*g*-PLA)₂₀-*b*-(PNB-*g*-PnBA)₁₈₀; red: entry 8 in table 1 (PNB-*g*-PLA)₄₀-*b*-(PNB-*g*-PnBA)₁₆₀; green: entry 9 in table 1 (PNB-*g*-PLA)₁₀₀-*b*-(PNB-*g*-PnBA)₁₀₀; black: entry 10 in table 1 (PNB-*g*-PLA)₂₀₀-*b*-(PNB-*g*-PnBA)₂₀₀; (e) red: entry 11 in table 1 (PNB-*g*-PLA)₅₀-*ran*-(PNB-*g*-PnBA)₅₀; blue: entry 12 in table 1 (PNB-*g*-PLA)₁₀₀-*ran*-(PNB-*g*-PnBA)₁₀₀; green: entry 13 in table 1 (PNB-*g*-PLA)₂₀₀-*ran*-(PNB-*g*-PnBA)₂₀₀; (f) black: entry 14 in table 1 (PNB-*g*-PLA)₁₆₀-*ran*-(PNB-*g*-PnBA)₄₀; red: entry 15 in table 1 (PNB-*g*-PLA)₁₃₀-*ran*-(PNB-*g*-PnBA)₇₀.



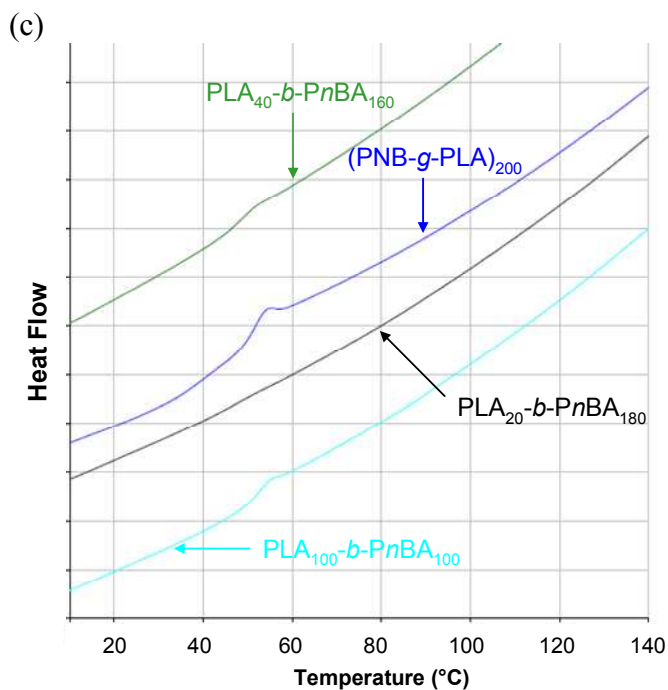
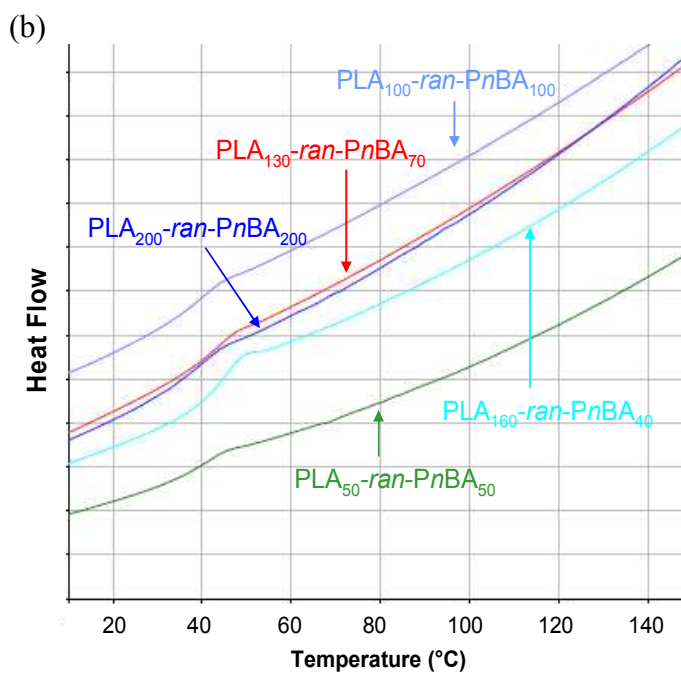


Figure S4. DSC traces of (a) macromonomer NB(PLA)4.7k and brush homopolymer (PNB-*g*-PLA)₂₀₀; (b) brush random copolymers (PNB-*g*-PLA)_x-*ran*-(PNB-*g*-PnBA)_y; (c) brush block copolymers (PNB-*g*-PLA)_x-*b*-(PNB-*g*-PnBA)_y.

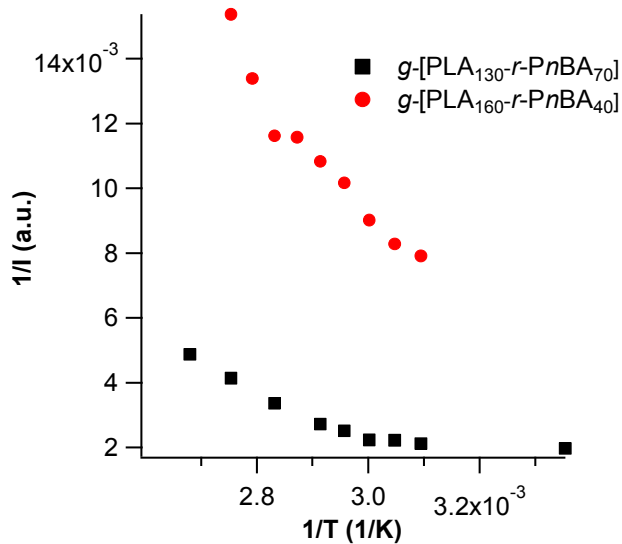


Figure S5. Inverse intensity of peak heights vs inverse temperature for asymmetric brush random copolymers.

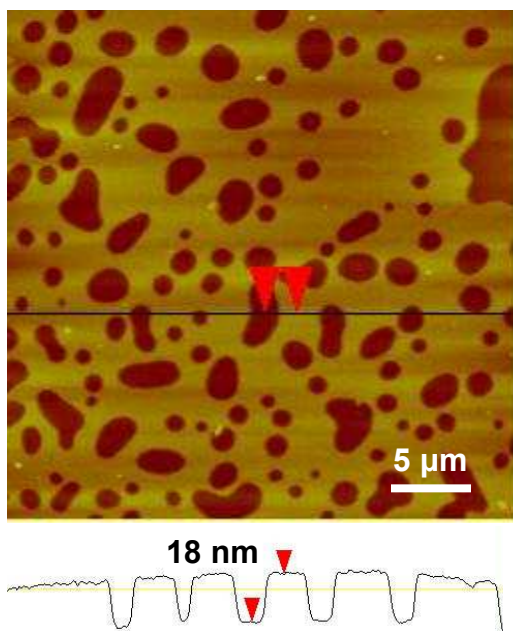


Figure S6. AFM height image of thin films of a mixture of two brush random copolymers, (PNB-*g*-PLA)₅₀-*ran*-(PNB-*g*-PnBA)₅₀ and (PNB-*g*-PLA)₁₀₀-*ran*-(PNB-*g*-PnBA)₁₀₀ (1:1), and its cross sectional analysis. A hole layer was formed in this case.

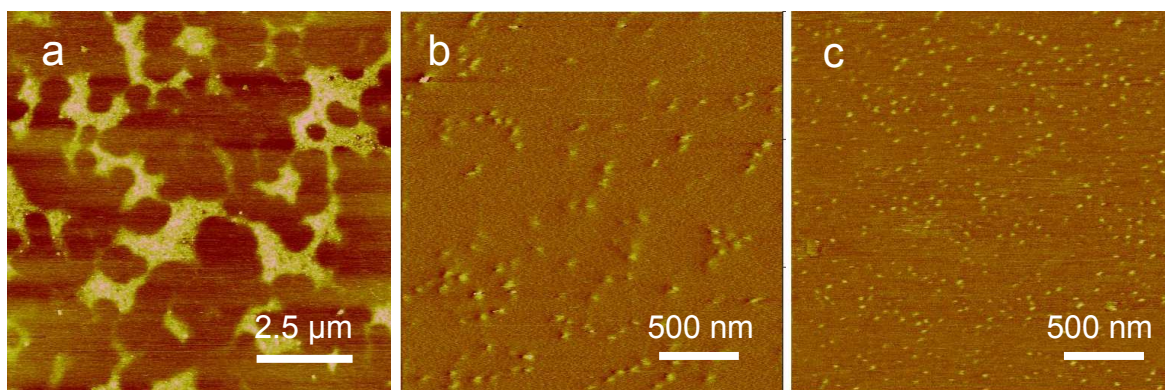


Figure S7. AFM phase images of brush block copolymer thin films (ca 120 nm) on silicon wafer: (a) (PNB-*g*-PLA)₁₀₀-*b*-(PNB-*g*-PnBA)₁₀₀; (b) (PNB-*g*-PLA)₁₃₀-*b*-(PNB-*g*-PnBA)₇₀; (c) (PNB-*g*-PLA)₁₆₀-*b*-(PNB-*g*-PnBA)₄₀.

References

- (1) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035–4037.
- (2) Matson, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 6731–6733.
- (3) Xia, Y.; Kornfield, J. A.; Grubbs, R. H. *Macromolecules* **2009**, *42*, 3761–3766.